

AD-A282 382

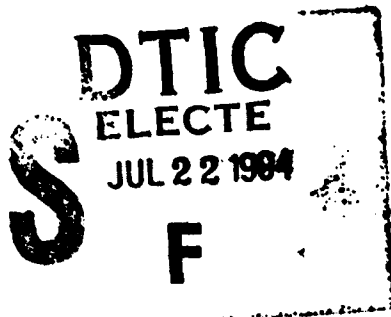


3
BMR-60298.02

A Bimonthly Report for:
SILICON-BASED BLUE LIGHT EMITTING DIODE

Submitted under:

Contract Number N00014-93-C-0176



Funded by:

Strategic Defense Initiative Organization

Covering the period:

1 November through 31 December 1993

This document has been approved
for public release and sale; its
distribution is unlimited.

*Original contains color
plates: All DTIC reproductions
will be in black and
white.

Submitted to:

Scientific Officer, NCCOSC RDTE DIV (NRaD)

53570 Silvergate Avenue

San Diego, CA 92152-5070

94-22750



1188

Submitted by:

Spire Corporation

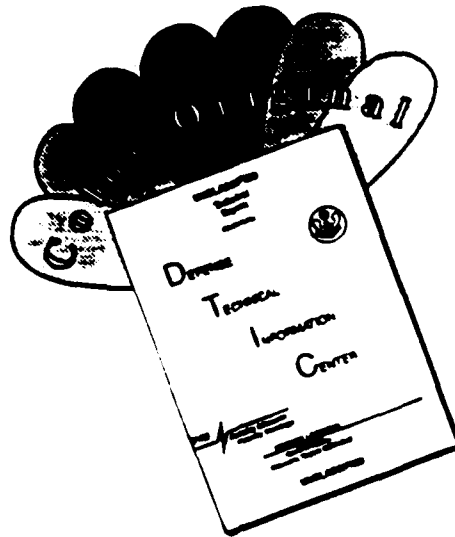
One Patriots Park

Bedford, MA 01730-2396

94 7 20 002

DTIC QUALITY INSPECTED 1

DISCLAIMER NOTICE



THIS DOCUMENT IS BEST QUALITY AVAILABLE. THE COPY FURNISHED TO DTIC CONTAINED A SIGNIFICANT NUMBER OF COLOR PAGES WHICH DO NOT REPRODUCE LEGIBLY ON BLACK AND WHITE MICROFICHE.

OVERALL OBJECTIVE

The overall goal of this program is to fabricate stable green/blue electroluminescent devices based on nanostructures of Si alloyed with group IV (such as carbon and germanium).

INTRODUCTION

During the past two years, optically excited visible-light emission¹ from electrochemically etched anodized silicon² has provided researchers with the possibility of fabricating a red-to-orange LED based on porous Si.³⁻⁶ A few groups have used semi-transparent Au as a solid state contact to porous Si to form Schottky diodes.^{4,5} Spire, under a SDIO funded SBIR program, has demonstrated a light-emitting device consisting of a heterojunction between electrochemically etched p-type porous Si and n-type transparent indium tin oxide (ITO). The use of ITO or other wide-bandgap semiconductors^{3,7} which are transparent to visible light has potential applications for visible LEDs and display panels.

PHASE I OBJECTIVE

The Phase I objective is to demonstrate green/blue photoluminescence from nanostructures of Si alloyed with group IV.

Why a stable blue/green emission from porous Si is hard to achieve - One of the major factors presently preventing the realization of stable blue-green light-emitting devices using porous Si material is the required limitation of the physical size of the Si nanostructures necessary to expand the bandgap into the blue wavelength range. The blue-green emitting crystallites formed in porous Si are presently too fragile and unacceptably susceptible to environmental effects during the processing steps required to fabricate materials. The constraints on microcrystalline dimensions for producing blue LEDs can be relaxed by creating alloys of Si which intrinsically possess larger energy gaps.

Method to obtain stable blue/green emission - We believe blue-green emission may be obtained by: a) increasing the base bandgap of the bulk material using chemical vapor deposition (CVD) of SiC and/or SiGe layers prior to forming quantum-sized structures. The initial increase in the bandgap of the pre-etched wafer would permit larger "quantum wires" or nanostructures to yield the energy gap required for blue- or green-emitting crystallites, or b) creating a SiC (SiGeC) phase by carbon (or C and Ge) **implantation** into red-emitting Si (and/or GeSi) nanostructures. This idea is a completely new concept that was developed recently as a result of an ongoing AF SBIR program which successfully demonstrated strong IR (1.54 μm) emission from Er-implanted Si nanostructures.

EXPERIMENTAL RESULTS

Epitaxial growth of SiC and SiGe by CVD - Growth of ternary Si epi is very complicated, thus we have begun our work with epitaxial growth of SiC and SiGe layers using Applied Materials CVD reactors. Our overall approach is shown in a flowchart in Figure 1.

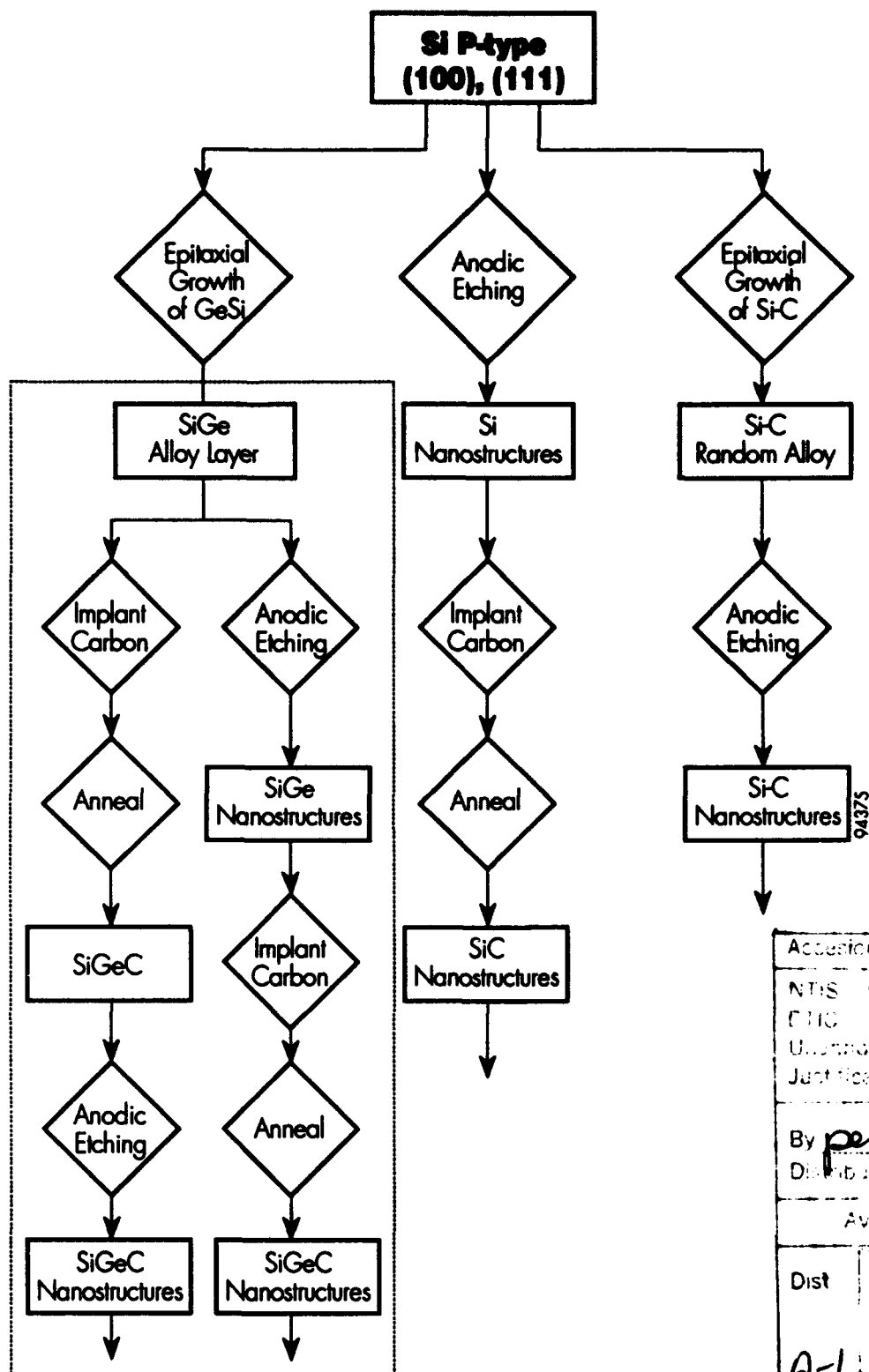


Figure 1 A flowchart detailing the four approaches we investigated to achieve green-blue emission from porous Si nanostructures

We started with SiGe epitaxial layers which were grown by high atmospheric-temperature CVD. Table I shows samples with SiGe layer thicknesses ranging from 500Å to 10 µm. Typical RBS results of a thin (<2000Å) and a thick (few microns) SiGe layer are shown in Figure 2.

The lattice mismatch of carbon (diamond structure) with Si is about 52%, therefore, we proposed to grow SiGeC instead of SiC layers on a Si substrate because the presence of Ge atoms could compensate the strain resulting from the Si and C mismatch.

To achieve blue-green emission from a SiGe epilayer, we carried out our investigation using two approaches: a) etch SiGe to form SiGe quantum confined structures, and then implant the nanostructures with carbon and, b) implant carbon into a SiGe epilayer to form a SiGeC phase and then perform anodic etching to form SiGeC porous structures. Table I shows samples with different SiGe epilayer thicknesses which were implanted with carbon. The material characteristics of these samples are presently being studied in collaboration with Dr. R. Fathauer and Dr. T. Pike at Jet Propulsion Laboratory. After completion of this analysis the samples will be anodically etched to form SiGeC nanostructures.

To ensure the success of our program, we have extensively examined the direct growth of SiC by CVD. We epitaxially grew Si layers, doped with carbon using methane gas, with nominal thicknesses of 8-10 µm. These layers were grown on several 2-inch and 4-inch B <111> Si wafers (See Table II) with various fluences of methane gas. We are now studying the SiC layers by Rutherford backscattering spectroscopy (RBS) to determine the amount of carbon and its effect on the material. We have etched some of these wafers by our standard anodic etching methods and have observed very strong red-emitting photoluminescence (PL), this red PL was stronger than any we have previously observed. We speculate that such a strong red emission may be from a rather impurity (metals) free Si epilayer. Note that bulk Si produced by standard processes contains trace elements with a large number of impurities including transition metals. Figure 3 shows a PL spectrum from the porous Si-C sample and Figure 4 and 5 are photographs of the same red-emitting porous sample showing that its emission is as strong as, or stronger than, that of a standard color PC monitor. Our bulk Si-C and porous Si-carbon structures are being studied further for their material and optical characteristics; the results will be detailed in a future report. So far, we have studied these samples by RBS, however, RBS is not sensitive to concentrations of carbon below 10%. Since we did not observe any carbon effect in our samples, we believe the concentrations were below 10%. We hope to determine the amount of carbon by PL.

A novel and simple approach for fabrication of green and blue nanostructures - The growth of a SiGeC phase has been limited by both the complexity and difficulty of the process and the time and funding limitations of the program. This motivated us to seek a new and easier method to form Si-based blue-green light-emitting materials.

We assumed that random alloys of SiGe or SiC (with concentrations of a few percent) are required in order to form porous nanostructures of SiC and SiGeC using standard Si processing. This idea was based on work developed at IBM for processing of GeSi. B. Meyerson at IBM has indicated that they have applied standard Si processing to group IV alloys for Si concentrations up to 80%.⁸ For that reason we were seeking to grow random Si alloys with concentrations above 80%. We assumed that very extensive work would be required to develop processes to etch SiC (50%/50%) and produce SiC nanostructures with quantum confined properties.

Table I *Summary of samples epitaxially grown with GeSi layers of various thicknesses and Ge concentrations.*

SILICON WAFERS	Sample ID	Si Epi	GeSi	%Ge	Si Epi	Carbon Implantation	
						Dose	Energy
	GER1044N	—	500Å	15%	—	1E17	100keV
	GER1023E	—	1000Å	10%	—	1E17	100keV
	GER1022E	—	2µm	10%	—	1E16 2E16	80keV 200keV
	T476	1000Å	2000Å	10%	2000Å	1E16	80keV
	D4662	—	4.72µm	18%	—	5E16	80keV
	GER 1021BE	—	1µm	10%	—	1E17	80keV
	GER1024E	—	300Å	10%	—		
	GER1046B	—	1300Å	11%	—		
	D4709	—	10µm	2.3%	—		

94511

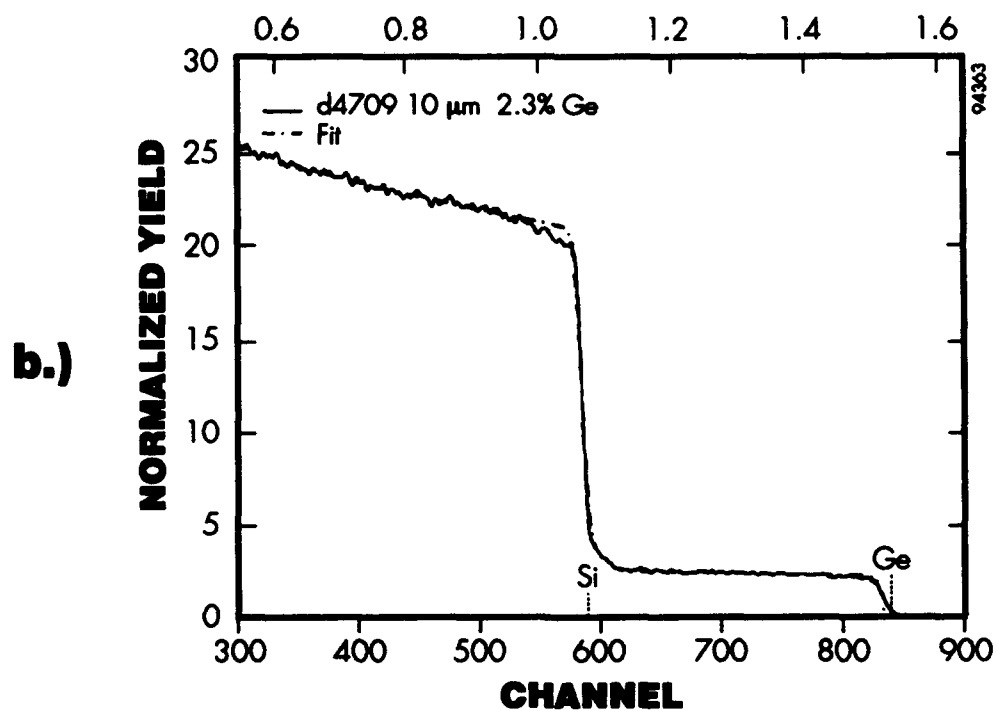
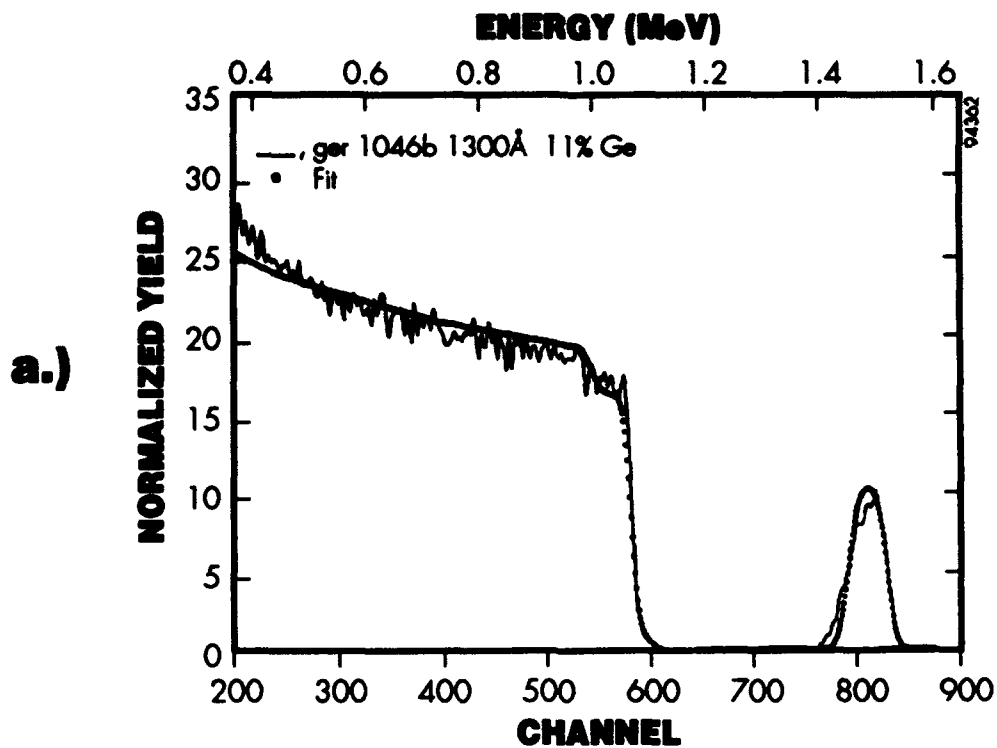


Figure 2 RBS (using the RUMP code) of epitaxially grown SiGe layers a) a thin layer approximately 1300Å thick, and b) a thick layer about 10 μm thick.

Table II *Summary of samples with Si-C layers epitaxially grown with various concentrations of methane gas.*

2" Substrates - B<111> .15 - .25 Ω cm				
Sample #	Depant s.p. (C)	Bake Temp	Hom. Thickness	Depant
F2017 CA CB	30% of max. methane flow rate	1053°C	8 μ m	Methane
4" Substrates - B<111> .002 - .005 Ω cm				
Sample #	Depant s.p. (C)	Bake Temp	Hom. Thickness	Depant
F2018 CA CB	50% of max. methane flow rate	1120°C	10 μ m	Methane
F2019 CB CC	70% of max. methane flow rate	1120°C	10 μ m	Methane
F2020 CC CE	85% of max. methane flow rate	1120°C	10 μ m	Methane
F2021 CA CC	100% of max. methane flow rate	1120°C	10 μ m	Methane

94512

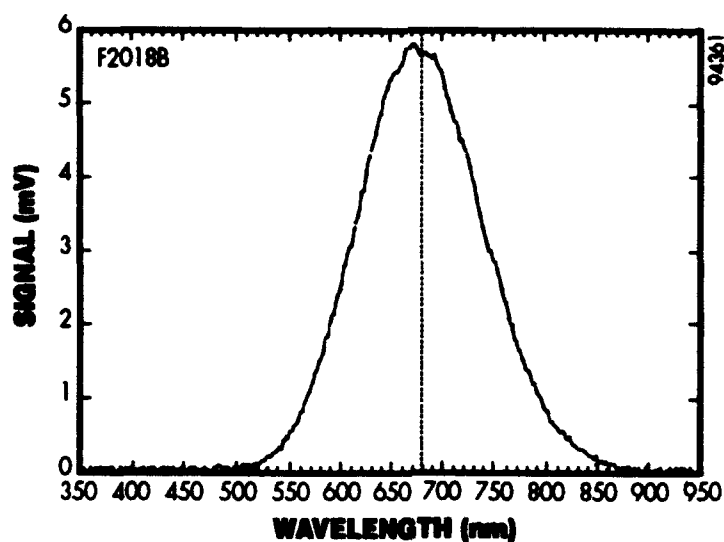


Figure 3 *PL spectrum from a Si-C porous structure fabricated from anodically-etched epitaxial Si-C.*

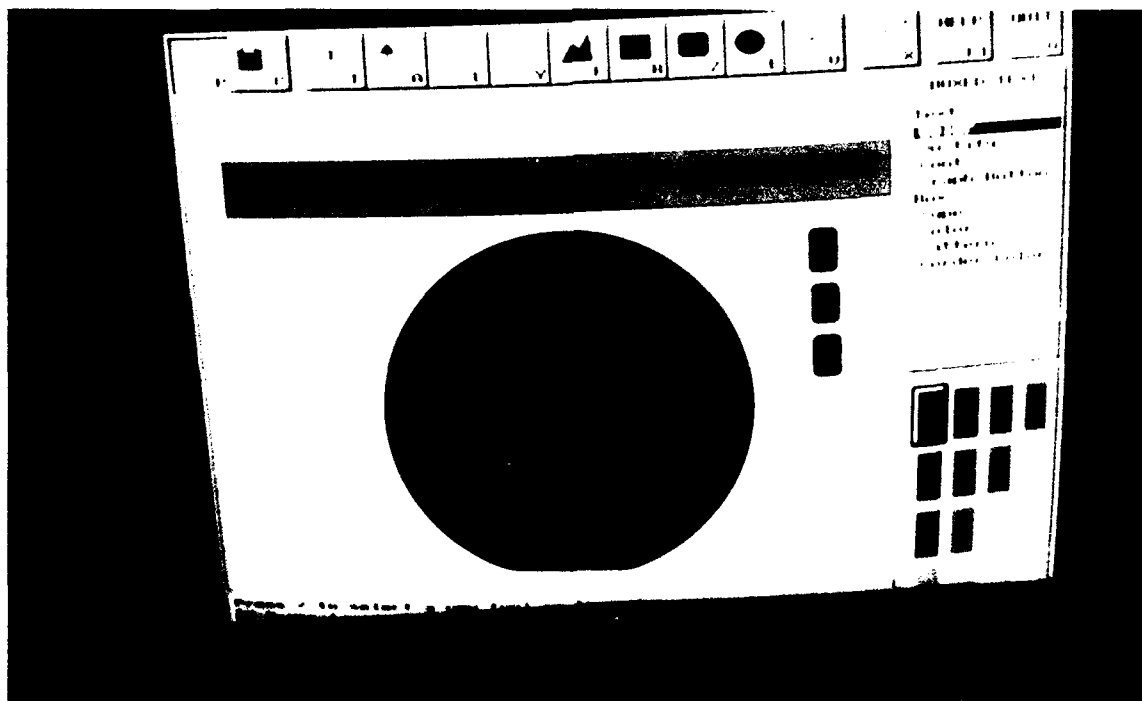


Figure 4 *Photograph showing a red-emitting porous Si-C sample, fabricated from an anodically-etched CVD grown Si-C layer, which was mounted on a color PC monitor in the dark to compare the uniform color and intensity of the sample.*

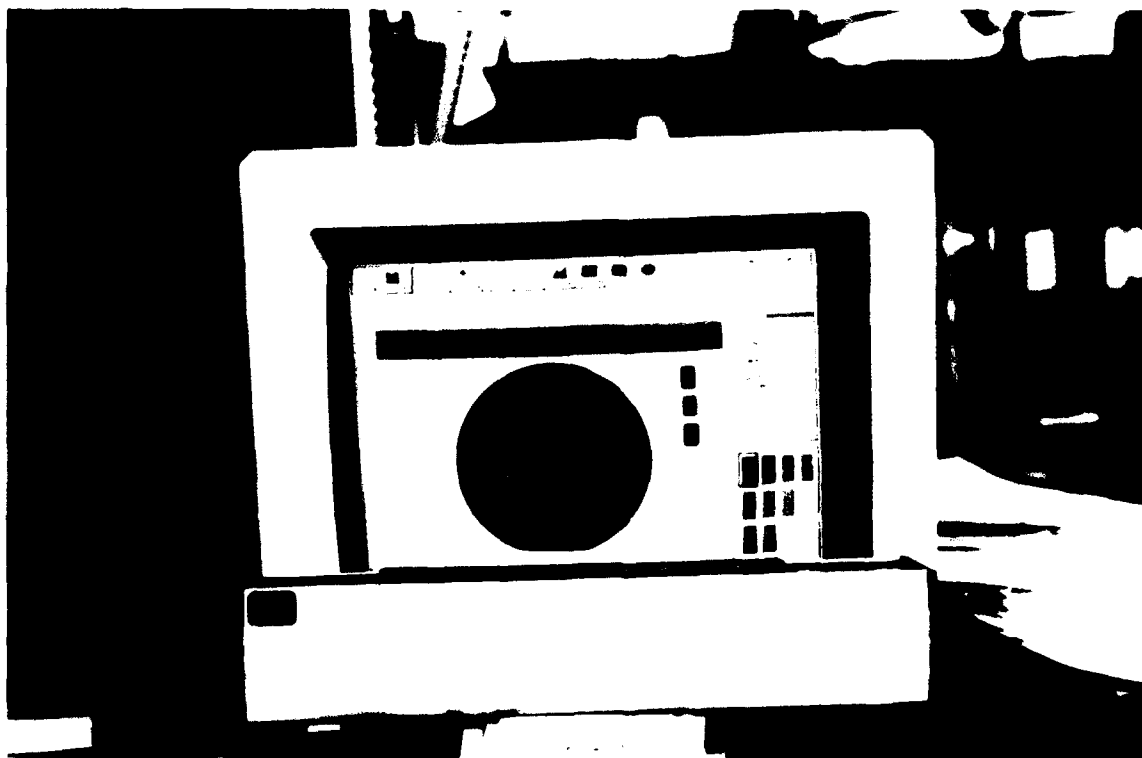


Figure 5 *Photograph showing a red-emitting porous Si-C sample, fabricated from an anodically-etched CVD grown Si-C layer, which was mounted on a color PC monitor in room light to compare the uniform color and intensity of the sample.*

In the course of Phase I work, we came to the idea that instead of modifying the bandgap of bulk Si-based materials, it would be easier to change/enlarge the bandgap of Si nanostructures. A simple way to test this concept, was to implant carbon into Si nanostructures in order to form Si-C or SiC quantum confined nanostructures. This idea was strengthened by an AF SBIR program in which we demonstrated for the first time strong room-temperature infrared ($1.54\mu\text{m}$) PL from erbium-implanted porous Si.

Thus, in addition to performing the Phase I tasks, we have also implanted carbon into numerous 3-inch p-type bulk Si and red-orange luminescent porous Si samples. Implantation was performed with doses ranging from 1×10^{16} to $1 \times 10^{17}/\text{cm}^2$ at energies from 50 keV to 140 keV using an NV-10-160 ion implanter. By first fabricating the porous material and then implanting carbon, we have eliminated the problem of epitaxial growth and etching Si-C and SiC materials.

FUTURE WORK

We are in the process of annealing the C-implanted SiGe, porous Si, and porous SiGe samples. These samples will be studied by transmission electron microscopy (TEM), PL and RBS.

REFERENCES

1. L.T. Canham, *Appl. Phys. Lett.* **57**, 1046 (1990).
2. R.L. Smith and S.D. Collins, *J. Appl. Phys.* **71** (8), R1 (1992).
3. F. Namavar, P. Maruska, and N.M. Kalkhoran, *Appl Phys. Lett.* **61**, 2514 (1992).
4. A. Richter, W. Lang, P. Steiner, F. Lozowski, and H. Sandmaier, *MRS* **246**, 209 (1991).
5. N. Koshida and M. Katsuno, *Appl. Phys. Lett.* **60**, 347 (1992).
6. T. Futagi, T. Matsumoto, *et al.*, *MRS* **283**, 389 (1993).
7. F. Namavar, N. Kalkhoran, and P. Maruska, U.S. Patent No. 5,272,355 (Dec 21, 1993).
8. B.S. Meyerson, Private Communication, 1991.

DISTRIBUTION

**Scientific Officer
Attn: Guy Beaghtler
NCCOSC RDTE DIV (NRaD)
53570 Silvergate Avenue, Room 2070
San Diego, CA 92152-5070**

**Office of Naval Research
Attn: Ms. Rebecca A. Taylor, Contracting Officer
Ballston Tower One
800 N. Quincy Street
Arlington, VA 22217-5660**

**Director, Naval Research Laboratory
ATTN: Code 2627
Washington, DC 20375**

**Defense Technical Information Center (2)
Building 5, Cameron Station
Alexandria, VA 22304-6145**

**Ballistic Missile Defense Organization
ATTN: T/IS
The Pentagon
Washington, DC 20301-7100**

**DCMAO Boston (LO)
Attn: Robert Muldoon
495 Summer Street
Boston, MA 02210-2138**